

Dist: A

AD-A28 147

PAGE -

Form Approved

OMB 0704-0188

Public report  
gathering and  
collection of  
Davis Highway



For response, including the time for reviewing instructions, send all correspondence to the Department of Defense, Office of Management and Administration, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and subject to the provisions of the General Regulations of the Department of Defense.

1. AGENCY

3. REPORT TYPE AND DATES COVERED

ANNUAL 01 May 93 TO 30 Apr 93

4. TITLE AND SUBTITLE

SPECTROELECTROCHEMICAL INVESTIGATIONS OF MOLTEN  
HALIDE SOLUTIONS

5. FUNDING NUMBERS

F49620-92-J-0222

61103D

3484/S2

6. AUTHOR(S)

Dr Gleb Mamantov

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Univ of Tennessee  
Dept of Chemistry  
552 Buehler Hall  
Knoxville, TN 37996-1600

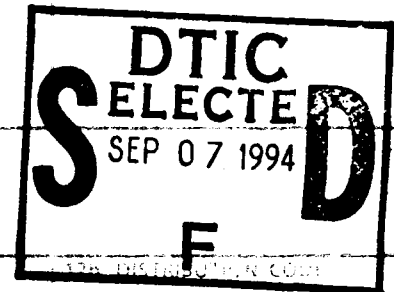
AEOSR-TR- 94 0500

9. SPONSORING MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NL  
110 Duncan Ave Suite B115  
Bolling AFB, DC 20332-0001

SPONSORING MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES



12a. DISTRIBUTION AVAILABILITY STATEMENT

Approved for public release;  
distribution unlimited.

A

13. ABSTRACT (Maximum 200 words)

The main objective of this research, performed by Ellen Kurt Hondrogiannis, a graduate student at the University of Tennessee, is to investigate the utility of the combination of spectroscopy and electrochemistry, or spectroelectrochemistry (SEC), for studies of redox processes in molten halides. The initial studies involved the use of UV-visible, Raman, and electron spin resonance SEC to identify the radical anion intermediate formed during the electrochemical reduction of tetrachloro-p-benzoquinone, or chloranil, in the basic (50 mole percent AlCl<sub>3</sub>) molten sodium chloroaluminate melt at 175 Degree C (2). This anion intermediate had not been detected in this melt previously, since cyclic voltammetry shows only one wave which had previously been attributed to a single two electron reduction to the dianion (2).

DTIC QUALITY INSPECTED 3

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION  
OF REPORT

(U)

18. SECURITY CLASSIFICATION  
OF THIS PAGE

(U)

19. SECURITY CLASSIFICATION  
OF ABSTRACT

(U)

20. LIMITATION OF ABSTRACT

(U)

Second Annual Technical Report


AF Grant F49620-92-J-0222

Spectroelectrochemical Investigations of Molten Halide Solutions

June 16, 1994

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

Gleb Mamantov  
Principal Investigator

SR 94-29001  


DTIC QUALITY INSPECTED 3

94 9 06 081

The main objective of this research, performed by Ellen Kurt Hondrogiannis, a graduate student at the University of Tennessee, is to investigate the utility of the combination of spectroscopy and electrochemistry, or spectroelectrochemistry (SEC), for studies of redox processes in molten halides. The initial studies involved the use of UV-visible, Raman, and electron spin resonance SEC to identify the radical anion intermediate formed during the electrochemical reduction of tetrachloro-p-benzoquinone, or chloranil, in the basic (<50 mole percent  $\text{AlCl}_3$ ) molten sodium chloroaluminate melt at  $175^\circ\text{C}$  (1). This anion intermediate had not been detected in this melt previously, since cyclic voltammetry shows only one wave which had previously been attributed to a single two electron reduction to the dianion (2).

UV-visible SEC was also used to study the electrochemical reduction of  $\text{NbCl}_5$  in the basic  $\text{AlCl}_3$ - $\text{NaCl}_{(\text{sat})}$  melt at  $175^\circ\text{C}$  (3). The SEC showed that  $\text{Nb}_6\text{Cl}_{18}$  ( $\text{Nb}^{2.33+}$ ) is electrochemically generated in the last reduction and that it can be oxidized through the  $\text{Nb}^{2.50+}$  cluster to the  $\text{Nb}^{2.67+}$  cluster. It was also shown that the  $\text{Nb}^{2.33+}$  cluster is generated in each of the first three waves. This formation is believed to be due to the slow disproportionation of  $\text{Nb}^{4+}$ , formed during the first reduction wave, to  $\text{Nb}^{5+}$  and  $\text{Nb}^{3+}$ , the latter of which probably decomposes to form the subvalent cluster.

UV-visible SEC was also used to study the behavior of  $\text{K}_2\text{ReCl}_6$  in the basic  $\text{AlCl}_3$ - $\text{NaCl}_{(\text{sat})}$  melt at  $175^\circ\text{C}$ . The initial cyclic voltammograms obtained for  $\text{K}_2\text{ReCl}_6$  solutions result in the formation of a new voltammetric wave at potentials more positive than the  $[\text{ReCl}_6]^{2-}$  reduction. After this wave grows in, the equilibrium cyclic voltammogram for a solution of  $[\text{ReCl}_6]^{2-}$  consisting of three reduction and two oxidation waves does not change. The new wave is believed to result from the  $[\text{Re}_2\text{Cl}_9]^{2-}/[\text{Re}_2\text{Cl}_8]^{2-}$  couple; the second broad wave probably results from the reduction of both  $[\text{ReCl}_6]^{2-}$  and  $[\text{Re}_2\text{Cl}_8]^{2-}$ . The very unstable  $[\text{ReCl}_6]^{3-}$  yields  $[\text{Re}_2\text{Cl}_8]^{2-}$ ,  $[\text{ReCl}_6]^{2-}$ , rhenium metal, and at least one other product. The presence of  $[\text{Re}_3\text{Cl}_{12-x}]^{4-x}$  is believed to result from the slow decomposition of  $[\text{Re}_2\text{Cl}_8]^{2-}$ . The  $[\text{Re}_3\text{Cl}_{12-x}]^{4-x}$  is stable in solution and is not reduced in the third reduction wave. The lack of decrease in the current in the third reduction even after 18 hours of electrolysis indicates that this step involves a catalytic regeneration of the starting material. X-ray powder diffraction of the particles produced in this step showed no evidence for rhenium metal. Further analyses of these particles using neutron activation, elemental analysis, inductively coupled plasma, and UV-visible reflectance and absorption spectroscopies did not aid in identifying this precipitate.

#### REFERENCES

1. E.M. Hondrogiannis, J.C. Coffield, D.S. Trimble, A.E. Edwards, and G. Mamantov, Appl. Spectrosc., 48, 406 (1994).
2. P.A. Flowers and G. Mamantov, J. Electrochem. Soc., 136, 2944 (1989).
3. K.D. Sienerth, E.M. Hondrogiannis, and G. Mamantov, J. Electrochem. Soc., 141, 1762 (1994).